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(54) **TiO₂-PIGMENT COATED WITH SMALL INORGANIC PARTICLES**
MIT KLEINEN, ANORGANISCHEN TEILCHEN BESCHICHTETES TiO₂-PIGMENT
PIGMENT DE TiO₂ REVETU DE PETITES PARTICULES INORGANIKUES

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• **DATABASE WPI Week 8626 Derwent Publications Ltd., London, GB; AN 86-165096 XP002025968 & JP 61 097 133 A (MITSUBISHI METAL ET AL.), 15 May 1986.**

• **DATABASE WPI Week 8706 Derwent Publications Ltd., London, GB; AN 87-039671 XP002025969 & JP 61 295 234 A (SUMITOMO CHEM. IND.), 26 December 1986**

• **DATABASE WPI Week 9204 Derwent Publications Ltd., London, GB; AN 92-028963 XP002025970 & JP 03 275 768 A (SHOWA DENKO), 6 December 1991**

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Description

BACKGROUND OF THE INVENTION

5 [0001] The present invention relates to a TiO_2 pigment particle having a surface coating of inorganic particles wherein improved light scattering efficiency of TiO_2 is achieved at a moderate to a high pigment volume concentration (PVC) when incorporated in coatings applications, and methods of accomplishing the same.

[0002] Inorganic pigments, and especially TiO_2 , are often incorporated in various polymers as whiteners, tinting agents or opacifiers. TiO_2 is particularly useful for these purposes because it scatters light very efficiently. However a problem encountered is that as the PVC increases in the polymer, the TiO_2 particles come close to or in contact with other TiO_2 particles which reduces the scattering efficiency of the TiO_2 , i.e., an optical crowding effect. Typically, scattering efficiency or scattering coefficient is measured by hiding power and tinting strength. While prior art techniques attempt to minimize the foregoing problem, they are deficient in one or more areas. For example, extenders have been added to paint formulations to space the TiO_2 to preserve its scattering efficiency, however, these extenders are difficult to distribute within the paint matrix to maximize the TiO_2 hiding power. Extenders are typically larger particles and/or in the form of aggregates and thus tend to increase the effective TiO_2 volume concentration and decrease scattering efficiency as they are added to replace paint resin content as described in F. Stieg, "The Effect of Extenders on the Hiding Power of Titanium Pigments", Official Digest, 1959, pp. 52-64.

[0003] Further, hydrous silica with high surface area can be precipitated onto the surface of the TiO_2 exhibiting some improvement in scattering efficiency at increasing PVC. However, the TiO_2 pigments with hydrous silica coatings with high surface area have a high oil absorption which degrades the paint film integrity, decreases a critical pigment volume concentration (CPVC) as defined hereinbelow and restricts a paint maker of flexibility in formulating paints. In addition, silicas such as fumed silica are composed of many primary particles which are highly aggregated and cannot be distributed uniformly on the TiO_2 surface.

[0004] Similarly, use of a polymer coating is expensive and difficult to accomplish and has resulted in severe agglomeration of the TiO_2 particles.

[0005] There is a need for a product that has improved scattering efficiency at moderate to high PVC. Concomitantly, there is a need for a TiO_2 having a low oil absorption so that the paint film integrity can be maintained. The present invention meets these needs.

SUMMARY OF THE INVENTION

[0006] In accordance with this invention there is provided:

a TiO_2 pigment having improved light scattering efficiency consisting essentially of TiO_2 pigment particles comprising substantially discrete inorganic particles having an average size within a range of about 5 to about 100 nm in diameter which are dispersed on the surface of the TiO_2 particles, and processes for preparing the same.

[0007] The composition and processes are characterized by some of the following advantages which cumulatively render the composition and processes preferable to compositions and processes previously employed:

1. improved scattering efficiency of TiO_2 is achieved at moderate to high PVC;
2. low oil absorption of the TiO_2 ;
3. provides a paint maker with flexibility in formulation;
4. dilution of TiO_2 content is minimized;
5. better dispersion and uniformity of the inorganic particles is achieved; and
6. equal hiding power can be achieved with less TiO_2 or improved hiding power can be achieved using the same amount of TiO_2 in end use applications.

DETAILED DESCRIPTION

[0008] The production of TiO_2 by the vapor phase oxidation of TiCl_4 and AlCl_3 is well known and disclosed in U.S. Patents 2,488,439, and 2,559,638, the teachings of which are incorporated herein by reference. The TiO_2 used to prepare the pigment can be of a conventional rutile or anatase variety, produced by either a chloride or a sulfate process. Preferably, the TiO_2 is prepared by the chloride process and a rutile crystal form. The TiO_2 particles used to prepare the pigments of this invention can be a base TiO_2 referred to herein as TiO_2 directly removed from oxidizing TiCl_4 and before any finishing steps and/or before any surface treatments are applied. In the sulfate process, base TiO_2 refers to TiO_2 before any surface treatments are applied. Alternatively, the TiO_2 particles used to prepare the pigments of this invention can be a finished TiO_2 referred to herein as TiO_2 subjected to conventional finishing steps and/or surface treated with hydrous oxides such as alumina, silica, zirconia or the like, or combinations of these materials, as described

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in, for example, U.S. Patent Re 27,818 and U.S. Patent 4,125,412, the teachings of which are incorporated herein by reference. The hydrous oxides can range from about 16 weight % or less of the total pigment product weight, and preferably 10 weight % or less. Contemplated equivalents include other white pigments such as zinc oxide, zinc sulfide, basic lead sulfate, basic lead carbonate, antimony oxide, lithopone or the like.

5 [0009] The inorganic particles used to coat the TiO_2 surface or its equivalent in carrying out the invention can be varied. Preferably, the inorganic particles do not substantially absorb visible light and do not adversely interact with other components in an end use application. One important aspect is the size of the inorganic particles (primary particles), i.e., it is desirable that the inorganic particles are smaller than the TiO_2 pigment particles. Typically, the average size is within the range of about 5 to about 100 nm in diameter, preferably about 7 to about 50 nm, and more preferably about 10 to about 35 nm. The inorganic particles form a non-continuous coating of a discrete particulate form and can be observed and measured by electron microscopy such as transmission electron microscopy. Examples of inorganic particles include, but are not limited to particles of the following inorganic materials including those in hydrated form: 10 oxides of silicon, titanium, zirconium, zinc, magnesium, aluminum, yttrium, antimony, cerium, and tin; sulfates of barium and calcium; sulfides of zinc; carbonates of zinc, calcium, magnesium, lead and mixed metals; nitrides of aluminum; phosphates of aluminum, calcium, magnesium, zinc, cerium and mixed metals; titanates of magnesium, calcium, aluminum and mixed metals; fluorides of magnesium and calcium; silicates of zinc, zirconium, calcium, barium, magnesium, mixed alkaline earths and naturally occurring silicate minerals and the like; aluminosilicates of alkali and alkaline earths, and naturally occurring aluminosilicates and the like; oxalates of calcium, zinc, magnesium, aluminum and mixed metals; aluminates of zinc, calcium, magnesium, and mixed alkaline earths; hydroxides of aluminum; diamond; 20 or the like and above mixtures or composites thereof. Mixtures used herein are a physical mixture of inorganic particles containing more than one type of particulate form. Composites used herein is intimate combinations of two or more inorganic materials in a single particle or any other combination wherein at least two distinct inorganic materials are present in an aggregate particle.

[0010] Preferred are silica, titanium dioxide, zirconium oxide, zinc oxide, magnesium oxide, aluminum oxide, tin oxide, calcium carbonate, magnesium carbonate, aluminum phosphate, calcium phosphate, aluminosilicates including alkali and alkaline earth aluminosilicates and naturally occurring aluminosilicate and the like, calcium silicates and naturally occurring silicate minerals and above mixtures or composites thereof.

[0011] More preferred are amorphous silica, hydrated forms of alumina, aluminosilicates including alkali and alkaline earth aluminosilicates, calcium silicates, titanium dioxide, calcium phosphate and calcium carbonate and above mixtures or composites thereof. Examples of silica are commercially available under the tradenames Ludox® colloidal silica which is available from E. I. du Pont de Nemours and Company, Nalcoag® which is available from Nalco Chemical Company, and Nyacol® which is available from Akzo Nobel.

[0012] The amount and size of inorganic particles will influence the surface area and thus impact the oil absorption of the product, as described hereinbelow. For example, larger size inorganic particles within the above prescribed ranges and/or fewer inorganic particles can be used to avoid or minimize increasing oil absorption. Typically, the inorganic particle is less than about 20 weight %, based on the total weight of the coated TiO_2 , preferably less than about 15 weight %, and more preferably less than about 10 weight %. The inorganic particles can be amorphous or crystalline and any shape is suitable such as spherical, equiaxial, rod-like or platelet. Preferably, the inorganic particle is equiaxial or spherical to minimize the oil absorption. It is desirable to have a substantially uniform distribution of the inorganic particles on the surface of the TiO_2 particles. The inorganic particles will be attracted to the TiO_2 surface by van der Waals' forces and may be further anchored to the TiO_2 surface by chemical bonding and/or by hydrous oxide coatings, if present as a topcoat.

[0013] Aggregates or agglomerates of inorganic primary particles are also useful as long as the average diameter of the aggregate or agglomerate is within the above prescribed size range of the inorganic primary particles. Aggregates are distinguished from agglomerates in that aggregates are held together by strong bonds such as fusion bonds and cannot be fragmented easily, while agglomerates are weakly bonded and can be broken up by high energy agitation.

[0014] These novel products of this invention have a surface area of less than about 33 m^2/g , preferably less than about 25 m^2/g and more preferably less than about 20 m^2/g , and an oil absorption of less than about 35, preferably less than about 25 and more preferably less than about 23.

50 [0015] In the process of this invention, a TiO_2 slurry is prepared with base TiO_2 . A colloidal suspension of inorganic particles, i.e., a sol is added to the TiO_2 slurry with sufficient mixing. Mixing can be carried out by any suitable means at a ratio of TiO_2 particles to inorganic particles which achieves the desired weight % of the final product. "Sol" is defined herein as a stable dispersion of colloidal particles in a liquid containing about 1 to 60% by weight inorganic particles as a dispersion in a liquid typically water. "Colloidal" is used herein to refer to a suspension of small particles which are substantially individual or monomeric particles small enough that they do not settle. It is preferred that the colloidal suspension is at the highest concentration at which the suspension is stable, typically about 14 to 50 wt%. These are commercially available or can be prepared as known in the art. For example, commercially available colloidal silica is about 40-50 wt% and commercially available colloidal alumina is about 20 wt%. Surprisingly, it has been found that 55

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both the particles in the TiO_2 slurry and the particles in the colloidal suspension are preferably both above or both below their respective isoelectric points to achieve a substantially uniform surface coating. The "isoelectric point" is used herein to refer to the pH at which particles have a neutral net charge. Opposite charges of the TiO_2 particles in the slurry and the inorganic particles in the colloidal suspension are also contemplated.

5 [0016] Optionally, hydrous oxides are precipitated onto the base TiO_2 particles or TiO_2 particles which have been coated with inorganic particles. Such hydrous oxides are silica, alumina, zirconia or the like. These may be added either before or after the addition of inorganic particles. If the hydrous oxides are added prior to addition of inorganic particles, then a filtering and washing step may be used prior to the addition of inorganic particles for colloidal suspen-
10 sions which may be sensitive to flocculation. It is preferred that the inorganic particles are added before the hydrous oxides are precipitated to further anchor the inorganic particles to the TiO_2 surface. For example, the method for precipitating the hydrous oxides is described in U.S. Patent Re 27,818 and U.S. Patent 4,125,412, the teachings of which are incorporated herein by reference. In precipitating the hydrous oxides, sodium silicate, potassium silicate or any other form of soluble silica is added and neutralized with acid such as HCl , H_2SO_4 , HNO_3 , H_3PO_4 or the like and then sodium aluminate is added and neutralized with acid. Other means of precipitating hydrous alumina are suitable, such
15 as neutralization of aluminum sulfate or aluminum chloride by base such as NaOH . The amount of hydrous oxides can vary from about 0 to 16 wt%, based on the weight of the total coated TiO_2 pigment. Preferred amounts are 0 to 8 wt% silica, more preferably 0 to 4 wt% silica, and 0 to 8 wt% alumina and more preferably about 0 to 3 wt% alumina. The order of addition is not particularly critical, however, the hydrous alumina precipitation, if added, is the last preferred addition. The conventional finishing steps such as filtering, washing, drying and grinding are known and are subse-
20 quently carried out. The resulting product is a dry, finished pigment which is useful for end use applications and/or can be used to prepare a slurry useful for end use applications. Methods for preparing slurries are known in the art, for example, as described in Canadian Patent 935,255, the teachings of which are incorporated herein by reference.

[0017] An alternative method of carrying out the invention is forming a mixture by combining a liquid medium such as water with the colloidal suspension of inorganic particles as described above in the presence of at least one disper-
25 sant to form a mixture. The dispersant can be either added simultaneously with water or subsequently. The dispersant can be selected from those described in U.S. Patent 5,393,510, the teachings of which are incorporated herein by reference. Examples of dispersants include alcohol amines such as 2-amino-2-methyl-1-propanol, 2,2',2''-nitrilotriethanol, 2,2'-iminobisethanol, 2-aminoethanol and the like, and 1-amino-2-propanol, polyacrylates, citric acid and tetrapotassium pyrophosphate (TKPP) and the like. Typically a combination of the above dispersants is preferred in
30 an amount of about 0.05 to about 5% based on the TiO_2 weight. The concentration of inorganic particles in the colloidal suspension is from about 10 to 60 weight % preferably about 30 to 60 wt%. It is preferable that the inorganic colloidal particles are well dispersed and not in an aggregate or flocculated form. As described above, both positive or both negative charges of the inorganic particles in the colloidal suspension and the TiO_2 particles are preferred to achieve a substantially uniform surface coating. To this mixture, finished TiO_2 is added with high shear mixing or milling as
35 described in greater detail in Canadian Patent 935,255, U.S. Patents 3,702,773 and 4,177,081, the teachings of which are incorporated herein by reference. In carrying out the mixing, a high shear mixer or mill such as a Waring blender, homogenizer, serrated disc type agitator, ball mill, sand mill, disc mill, pearl mill, high speed impeller mill or the like can be used. Specific speed characteristics depend on equipment, blade configuration, size, etc., but can be determined readily by one skilled in the art. Total solids content of the resulting slurry is above about 50% by weight, and above
40 70% by weight is preferred.

[0018] In yet another embodiment, inorganic particles are formed in the presence of TiO_2 . A TiO_2 slurry is formed and reagents are added to generate and to deposit a surface coating of the inorganic particles within the prescribed size range. It is preferable that the TiO_2 is subjected to washing prior to formation and deposition of the inorganic particles. Hydrous oxides can be added either before or after the formation of the inorganic particles. For example,
45 calcium carbonate may be formed in-situ by the carbonation of hydrated lime, calcium hydroxide. In carrying out the process, CO_2 gas and a TiO_2 and calcium hydroxide slurry are mixed at high speed, high shear as described in the previous embodiment. A slight excess of CO_2 is useful to complete the reaction rapidly.

[0019] The resulting improved TiO_2 pigment product is suitable for use in coating applications for example in architectural coatings, industrial coatings, paper coatings, and in paper, paper laminates, plastics and inks. The enhanced
50 scattering efficiency is best demonstrated in coatings with greater than 15% PVC, preferably greater than 20% PVC, and more preferably greater than 25%. PVC is expressed as a percentage and represents the sum of the pigment volume and extender volume, if present, divided by the sum of the resin volume, extender volume, if present, and pigment volume. Examples include but are not limited to semi-flat interior paints, such as eggshell or satin, and exterior flat paints, and industrial coil coatings. It will be appreciated by those skilled in the art that the semi-flat paints are
55 formulated below the critical pigment volume concentration (CPVC) to maintain film integrity for scrub and stain resistance. The exterior flat paints are formulated at or near the CPVC to maintain film integrity and to obtain maximum weatherability. The CPVC is defined herein as the specific PVC at which the vehicle demand of the pigment is precisely satisfied, as described in greater detail in C. Martens, "Technology of Paints, Varnishes and Lacquers", 1968, pp.

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498-500, the teachings of which are incorporated herein by reference. This concentration is critical because above or below this value the properties of a formulation change dramatically. The TiO₂ paint formulations are made by techniques known in the art and are described in greater detail in Paint and Surface Coating - Theory and Practice, edited by R. Lambourne, Ellis Harwood Limited (1987) and Principles of Paint Formulation, edited by R. Woodbridge, Blackie & Sons Limited (1991), the teachings of which are incorporated herein by reference.

[0020] To give a clearer understanding of the invention, the following Examples are construed as illustrative and not limitative of the underlying principles of the invention in any way whatsoever.

EXAMPLESCOMPARATIVE EXAMPLE 1

[0021] A finished TiO₂ slurry was made by dispersing 1000 g of an enamel grade TiO₂ having hydrous oxide coatings of silica and alumina in 295 g of water containing dispersants using a high speed, high shear mixer with a 2 inch blade at 2000 RPM for 15 minutes. Final solids content of the slurry was 76.5% by weight. The pH was 9.

[0022] A latex emulsion paint concentrate was prepared using a Rhoplex® HG-74M acrylic copolymer vehicle, available from Rohm & Haas Company, modified for compability with the finished TiO₂ slurry. The paint concentrate was made without incorporating any TiO₂ and was tinted with a green tinting agent. As formulated, the paint concentrate contained 32% by weight solids.

[0023] 18.23 g of the TiO₂ slurry was combined with 46.77 g of the latex emulsion paint concentrate and shaken 5 minutes to make a paint with a PVC of 20% in the dried paint film, based on a pigment density of 4.0 g/cm³ and a resin density of 1.07 g/cm³. Similar combinations of pigment slurry and paint concentrate were combined to make paints containing 30 and 35% PVC. These paints were drawn down using a 0.002 inch Bird applicator onto black and white substrates and air dried. The green (Y) reflectance values over black and white were measured and the Kubelka-Munk K/S values calculated and reported in Table 1. The green (Y) reflectance value was measured using a Hunter Lab Scan reflectance spectrophotometer. The Kubelka-Munk (K/S) values were calculated using equations found in D. B. Judd and G. Wyszecki, "Color in Business, Science and Industry", 2nd ed., John Wiley & Sons, NY, 1963, pp. 396-397, the teachings of which are incorporated herein by reference.

EXAMPLE 2

[0024] The same enamel grade TiO₂ (910 g), was dispersed as in Comparative Example 1 in about 160 g of water containing dispersants and 225 g of a 40 wt% dispersion of colloidal silica in water, (Ludox® AS-40 colloidal silica, nominal particle size 22 nm, available from DuPont). The final slurry contained 76.5 wt% solids. On a dry weight basis, the pigment was comprised of 9% SiO₂ derived from colloidal silica. It had a calculated density of 3.73 g/cm³ (based on a silica density of 2.2 g/cm³). Green tinted paints were made as in Comparative Example 1 at PVCs of 20, 30, and 35% with adjustment for the lower pigment density. K/S values were obtained from drawdowns on black and white substrates. Results are in Table 1.

EXAMPLES 3-4

[0025] Similar combinations of Ludox® AS-40 and TiO₂ were made as in Example 2 to produce slurries of pigments comprised of 4.5% and 2.5% SiO₂ derived from colloidal silica (calculated pigment densities were 3.86 and 3.92 g/cm³, respectively). Slurry wt% solids were 76.5%. Green tinted paints at 20, 30, and 35% PVCs were made as in the above Examples and K/S values were similarly obtained. Results are in Table 1.

[0026] Tinting strengths were calculated at each PVC for Examples 2-4 relative to the Comparative Example 1 by taking the ratio of K/S of the Comparative Example divided by K/S for the Examples 2-4. At any particular PVC, K is constant due to a constant concentration of green pigment. Thus, tinting strength is the scattering coefficient, S, normalized to the Comparative Example. See Table 1. The higher tinting strengths of Examples 2-4 than of Comparative Example 1, despite the lower contents of TiO₂ in the paint, demonstrates the improvements in scattering coefficient.

TABLE 1

K/S VALUES AND RELATIVE TINTING STRENGTHS			
	K/S values		
	PVC = 20%	PVC = 30%	PVC = 35%
Comparative Example 1	0.140	0.108	0.100

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TABLE 1 (continued)

K/S VALUES AND RELATIVE TINTING STRENGTHS			
	K/S values		
	PVC = 20%	PVC = 30%	PVC = 35%
Example 2	0.137	0.100	0.088
Example 3	0.132	0.102	0.091
Example 4	0.134	0.103	0.094
	Relative Tinting Strength		
	PVC = 20%	PVC = 30%	PVC = 35%
Comparative Example 1	100%	100%	100%
Example 2	102%	108%	114%
Example 3	106%	106%	109%
Example 4	104%	104%	106%

EXAMPLES 5

[0027] 4245 ml of water and 1539 g of base TiO_2 prepared by the chloride process from TiCl_4 , were combined and heated to 90°C with stirring. The pH was raised to 11 with 165 ml of 10% NaOH. 450 g of Ludox® TM-50 colloidal silica dispersion containing 50% by wt SiO_2 with a nominal particle size of 22 nm available from DuPont was added. After stirring 10 min, 267.9 g of sodium silicate solution containing 28% by weight SiO_2 and with a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 3.2 was added. After stirring 10 min, 8% HCl in water was added at a rate of 7 ml/min until the pH reached 7. After 45 minutes at pH about 7 and 90°C , 144 g of sodium aluminate solution was added simultaneously with 380 ml of 8% HCl thus maintaining the pH at 7. After further stirring for 30 minutes the pH was lowered to 6 with HCl and the product was filtered, washed and dried. A second preparation was conducted under the same conditions and the products were combined and ground in a fluid energy mill. The final product was analyzed by x-ray fluorescence and found to contain 2.66% by weight Al_2O_3 , 15.55% by weight SiO_2 . Density measured by helium pycnometry was 3.56 g/cm^3 . Oil absorption was 32.5.

[0028] Hiding power is given in Table 2 and compared to a conventional enamel grade titanium dioxide (C2) with low oil absorption and low scattering efficiency, and to a conventional high oil absorption grade with moderate scattering efficiency used in flat paints typically formulated above the CPVC (C3). The product of Example 5 has a moderate oil absorption and improved hiding power. Hiding power measurements were made as described by J. E. McNutt and H. L. Ramsay in *American Paint and Coatings Journal*, April, 1988, p. 46, by the weight drawdown method in an acrylic emulsion resin system (Rhoplex® Multilobe 200 100% acrylic binder) using an average of 3 drawdowns. PVCs were calculated based on the measured TiO_2 pigment densities. No extender pigments and no colored pigments were included. The TiO_2 product is the only pigment present. Hiding power was determined using Y, the green reflectance measured over black and white backgrounds. Hiding power is expressed as scattering efficiency, S, in units of m^2/g of product.

TABLE 2

SCATTERING EFFICIENCY OF TiO_2 PRODUCT IN AN ACRYLIC EMULSION RESIN			
	O. A.*	S (m^2/g)	S (m^2/g)
		25% PVC	35% PVC
Example 5	32.5	0.363	0.320
Example 6	19	0.350	0.297
Example 7	18	0.336	0.287
Example 8	17	0.330	0.276
C2	16-18	0.303	0.253
C3	37	0.326	0.295

* Oil Absorption (ASTM Designation D281): The oil absorption value obtained gives information about the vehicle demand of the pigment when it is used in a paint and aids in paint formulation.

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[0029] In a dry coating application (a paint film) formed from a latex emulsion, formulated below the CPVC and comprised of the product of these embodiments but with no extenders, the hiding power (expressed as scattering efficiency, S , in units of square meters per gram [m^2/g] of product of this invention) is greater than $0.31 \text{ m}^2/\text{g}$ at 25% PVC and greater than $0.26 \text{ m}^2/\text{g}$ at 35 PVC, and preferably greater than $0.33 \text{ m}^2/\text{g}$ at 25 % PVC and preferably greater than $0.28 \text{ m}^2/\text{g}$ at 35 % PVC.

EXAMPLE 6

[0030] 8520 ml of water and 3080 g of the base TiO_2 used in Example 5 were combined and heated to 74°C while stirring. 76 ml of 10% NaOH was added increasing the pH to 9.5. 110 g of sodium silicate was added and stirred 10 minutes. 607 g of Ludox® TM-50 was added and stirred 15 minutes. Another portion of 110 g of sodium silicate was added and stirred. 8% HCl was added at about 7 ml/min until the pH reached about 7. After stirring at 75°C for 60 min, 265 g of sodium aluminate solution and 720 ml of 8% HCl were added simultaneously. The slurry was stirred an additional 30 min at 75°C , pH was lowered to 6, and the product was subjected to conventional finishing steps as described in Example 5. The product contained 2.43% Al_2O_3 and 10.04% SiO_2 , density was 3.63 g/cm^3 and oil absorption was 19. Surface area was $25.2 \text{ m}^2/\text{g}$ as measured by the nitrogen BET method.

[0031] Scattering efficiency is shown in Table 2. This product has a low oil absorption and a high hiding power.

EXAMPLE 7

[0032] The procedure used in Example 6 was followed except that 290 g of Ludox® TM-50 was used and 8% HCl was added at 5.5 ml/min. The product contained 2.6% Al_2O_3 , 5.9% SiO_2 ; it had a density of 3.80 g/cm^3 , an oil absorption of 18 and a surface area of $19.7 \text{ m}^2/\text{g}$.

[0033] Scattering efficiency is shown in Table 2. This product has a low oil absorption and a high hiding power.

EXAMPLE 8

[0034] The procedure used in Example 7 was followed except that 290 g of colloidal silica as a 50% by weight dispersion in water having a particle size of nominally 35 nm diameter was used instead of Ludox® TM-50. The final TiO_2 product contained 2.53% Al_2O_3 , 5.95% SiO_2 , with a density of 3.80 g/cm^3 and an oil absorption of 16.8.

[0035] Scattering efficiency is shown in Table 2. This product has a low oil absorption and a high hiding power.

EXAMPLE 9

[0036] The procedure used in Example 7 was followed except that 161 g of Ludox® TM-50 was used. The product contained 2.43% Al_2O_3 and 4.17% SiO_2 , had a density of 4.04 g/cm^3 , a surface area of $15.3 \text{ m}^2/\text{g}$ and an oil absorption of 19.7.

EXAMPLE 10

[0037] 8520 ml of water and 3080 g of the base TiO_2 used in Examples 5-9 were combined and heated with stirring to 90°C . The pH was adjusted to 10 and 400 g of Ludox® TM-50 was added and stirred 15 min. Then 220 g of sodium silicate was added, stirred 10 min and 8% HCl addition begun at a rate of 7 ml/min. After pH reached 7, HCl addition was stopped and stirring continued for 45 min at 90°C . Then 265 g of sodium aluminate and 740 ml of 8% HCl were added simultaneously. The slurry was stirred for an additional 30 min as the temperature dropped from 86 to 70°C . The pH was decreased to 6 by HCl addition and the product was filtered washed and dried. After grinding, the product contained 2.56 Al_2O_3 , 7.54% SiO_2 . Surface area was $16.2 \text{ m}^2/\text{g}$, density was 3.95 g/cm^3 , and oil absorption was 22.6.

[0038] The methods used to measure scattering efficiency in Examples 5-8 were repeated. Results are shown below in Table 3.

EXAMPLE 11

[0039] The procedure in Example 10 was followed except that the colloidal silica from Example 8 was used. The product contained 2.47 Al_2O_3 , 7.47% SiO_2 . Surface area was $18.1 \text{ m}^2/\text{g}$, density was 3.92 g/cm^3 , and oil absorption was 20.6. Results are shown in Table 3.

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TABLE 3

Scattering Efficiency, S, (m ² /g) with no extenders:		
PVC%	Example 10	Example 11
18.8	0.370	0.339
23.4	0.343	0.318
27.9	0.334	0.300
32.9	0.288	0.270
37.8	0.265	0.237

EXAMPLE 12

[0040] 283 ml of water and 102.6 g of the base TiO₂ in Examples 5-11 were combined and stirred. This was heated to 90°C and pH adjusted to about 11. 15 g of Ludox® TM-50 was added, stirred 10 min and then 8.93 g of sodium silicate was added and stirred 10 min. A solution of 4% by weight HCl was added at about 0.5 ml/min until the pH reached 7. After further stirring at 90°C and pH about 7, a small sample was removed, filtered, washed and dried. Transmission electron micrographs and scanning electron micrographs show the product morphology as discrete silica particles, approximately 20-25 nm in diameter, attached to the surface of the rutile titanium dioxide particles. SiO₂ derived from colloidal silica was about 6-7 wt %. To the remaining major portion of the reaction slurry, 9.6 g of sodium aluminate and 27.4 ml of 8% HCl were added simultaneously. The pH was adjusted to 7 and the slurry stirred at about 75°C for 30 min. The pH was then adjusted to about 6 and the final product was filtered, washed, and dried. The product contained 2.77% Al₂O₃, 8.46% SiO₂, and 88.76% TiO₂ (normalized to 100%).

EXAMPLE 13

[0041] 800 ml of water and 200 g of the base TiO₂ used in Examples 5-12 were combined and stirred. The slurry was filtered and washed with water. Half of the resulting wet filter cake was resuspended in water with stirring to a total volume of 400 ml. The pH was adjusted to 3.5 with HCl. 40 g of Dispak® 23N4-20 colloidal alumina dispersion available from Vista Chemical Company was added. This was then heated to 40°C and pH was adjusted to 10 with 10% NaOH. The slurry was further heated to 60°C and 5.4 g of sodium silicate solution (28wt.% SiO₂) was diluted in 20 ml of water and added to the TiO₂ slurry. The pH was adjusted to 9 and the slurry was stirred for 5 min. The slurry was then adjusted to pH 7, and the product recovered after filtering, washing and drying. The product was analyzed 9.1% Al₂O₃, 1.4% SiO₂ and 89.4% TiO₂ (normalized).

EXAMPLE 14

[0042] 50 g of Ti-Pure®, R-706, available from DuPont was dispersed in 150 ml of water at room temperature and stirred vigorously in a high shear, high speed mixer. 3.0 g of Ca(OH)₂ was added. While continuing high shear mixing, carbon dioxide was bubbled into the slurry at approximately 300 ml/min for 5 minutes as the pH decreased to about 6.5. The slurry was filtered, washed with a small amount of water and dried at 115°C. Transmission electron micrographs of the product show crystallites of calcium carbonate, roughly equiaxial in shape and typically 20 to 40 nm across which were distributed on the surface of the TiO₂ particles. When analyzed by x-ray fluorescence, the composition was 87.9% TiO₂, 2.48% Al₂O₃, 2.69% SiO₂ and 4.38% CaO (analyzed as the oxide). Weight loss measured with a thermogravimetric analyzer in the temperature range from 500 to 750°C demonstrated that most of the calcium was present as CaCO₃. Surface area was 13.3 m²/g.

EXAMPLE 15

[0043] 8500 ml of water and 3000 g of base TiO₂ were combined and heated to 60°C while stirring. 8 ml of 10% NaOH was added increasing the pH to about 9. 315 g of Ludox® HS-40 colloidal silica available from DuPont was added. Ludox® HS-40 is a 40 wt.% silica dispersion of 12 nm diameter silica particles. After stirring 15 minutes at 70°C, 225 g of sodium silicate solution was added. After stirring 10 minutes, 8% HCl solution was added at about 10 ml/min. After addition of 220 ml, pH was 8.5 and addition was stopped. After 30 minutes stirring at 70°C, additional HCl was added to bring pH to 7.5. 265 g of sodium aluminate solution and 715 ml of 8% HCl were added simultaneously. The pH was 7.5 after these additions. After 30 minutes stirring, pH was lowered to 7.0 and the product was filtered, washed and dried. The product was analyzed to contain 91.1% TiO₂, 2.8% Al₂O₃ and 6.1% SiO₂ (normalized to 100%).

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Oil absorption was 24.2. Scattering coefficients were measured: 0.384 m²/g at 14.7% PVC and 0.327 m²/g at 23.5% PVC and 0.265 m²/g at 34.1% PVC.

EXAMPLE 16

[0044] Dry base TiO₂ (950 grams) is dispersed by slowly adding it to a suspension containing Ludox® AS-40 colloidal silica (125 grams), water (175 grams) and dispersants while stirring with a high speed, high shear impeller. The pH is between 8 and 9. Stirring is continued for about 20 minutes. 84 grams of water is added so that the resulting slurry product contains about 75% solids by weight. On a dry weight basis, the slurry product comprises about 5% SiO₂ derived from the colloidal silica dispersion.

[0045] Having thus described and exemplified the invention with a certain degree of particularity, it should be appreciated that the following Claims are not to be limited but are to be afforded a scope commensurate with the wording of each element of the Claims and equivalents thereof.

Claims

1. A TiO₂ pigment consisting essentially of TiO₂ particles having (a) substantially discrete inorganic particles having an average diameter size within the range of about 5 to about 100 nm dispersed on the surfaces of the TiO₂ particles in an amount of less than 20 wt.% based on total pigment weight, and (b) a top-coating comprising a hydrous oxide selected from the group consisting of silica, alumina, zirconia, and mixtures thereof.
2. A TiO₂ pigment consisting essentially of TiO₂ particles having (a) a surface-coating comprising a hydrous oxide selected from the group consisting of silica, alumina, zirconia, and mixtures thereof, and (b) substantially discrete inorganic particles having an average diameter size within the range of about 5 to about 100 nm which are dispersed on the surface of the hydrous oxide surface-coating in an amount of less than 20 wt.% based on total pigment weight.
3. The TiO₂ pigment of claim 1 or 2, wherein the inorganic particles are selected from the group consisting of oxides of silicon, titanium, zirconium, zinc, magnesium, aluminum, yttrium, antimony, cerium, and tin; sulfates of barium and calcium; sulfides of zinc; carbonates of zinc, calcium, magnesium, lead, and mixed metals; nitrides of aluminum; phosphates of aluminum, calcium, magnesium, zinc, and cerium; titanates of magnesium, calcium, and aluminum; fluorides of magnesium and calcium; silicates of zinc, zirconium, calcium, barium, magnesium, mixed alkaline earth metals and naturally occurring silicate minerals; aluminosilicates of alkali and alkaline earth metals; naturally occurring aluminosilicates; aluminates of zinc, calcium, magnesium, and mixed alkaline earth metals; hydroxides of aluminum; diamond; and mixtures or composites of the foregoing particles.
4. The TiO₂ pigment of claim 1 or 2, wherein the inorganic particles have an average diameter size within the range of 7 to 50 nm.
5. The TiO₂ pigment of claim 1 or 2, wherein the amount of inorganic particles is up to 15 wt.% and the amount of hydrous oxides is up to 16 wt.% based on total pigment weight.
6. The TiO₂ pigment of claim 1 or 2, wherein the amount of inorganic particles is up to 10 wt.% and the amount of hydrous oxides is up to 16 wt.% based on total pigment weight.
7. The TiO₂ pigment of claim 6, wherein the inorganic particles are selected from the group consisting of silica, alumina, calcium carbonate, and mixtures or composites thereof.
8. The TiO₂ pigment of claim 7, wherein the pigment has an oil absorption of less than 35.
9. The TiO₂ pigment of claim 1 or 2, wherein the inorganic particles comprise silica particles in an amount up to 10 wt.% based on total pigment weight, and the hydrous oxides comprise up to 4 wt.% silica and up to 3 wt.% alumina based on total pigment weight.
10. The TiO₂ pigment of claim 9, wherein the pigment has an oil absorption of less than 25.
11. The TiO₂ pigment of claim 9, wherein the pigment has a light scattering coefficient greater than 0.31 m²/g at 25%

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pigment volume concentration and greater than 0.26 m²/g at 35% pigment volume concentration.

12. A TiO₂ pigment slurry comprising the TiO₂ pigment of claim 1 or 2, wherein the slurry has a TiO₂ pigment solids content above 50 wt.%.
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13. A process for preparing a TiO₂ pigment, comprising the steps of:

(a) mixing a slurry of TiO₂ particles with a colloidal suspension of inorganic particles, wherein the TiO₂ particles and the colloidal particles are both above or below their respective isoelectric points such that substantially discrete inorganic particles having an average diameter size within the range of about 5 to about 100 nm are dispersed onto the surfaces of the TiO₂ particles in an amount of less than 20 wt.% based on total pigment weight; and
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(b) precipitating a hydrous oxide selected from the group consisting of silica, alumina, zirconia, and mixtures thereof onto the TiO₂ particles resulting from step (a).
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14. A process for preparing a TiO₂ pigment, comprising the steps of:

(a) precipitating a hydrous oxide selected from the group consisting of silica, alumina, zirconia, and mixtures thereof onto the surfaces of TiO₂ particles to form surface-coatings, and
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(b) mixing a slurry of the surface-coated TiO₂ particles with a colloidal suspension of inorganic particles, wherein the TiO₂ particles and the colloidal particles are both above or below their respective isoelectric points such that substantially discrete inorganic particles having an average diameter size within the range of about 5 to about 100 nm are dispersed onto the surface-coated TiO₂ particles in an amount of less than 20 wt.% based on total pigment weight.
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15. A process for preparing a TiO₂ pigment, comprising the steps of:

(a) mixing a slurry of TiO₂ particles with reagents to form in-situ substantially discrete inorganic particles having an average diameter size within the range of about 5 to about 100 nm, wherein the inorganic particles are dispersed onto the surfaces of the TiO₂ particles in an amount of less than 20 wt.% based on total pigment weight; and
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(b) precipitating a hydrous oxide selected from the group consisting of silica, alumina, zirconia, and mixtures thereof onto the TiO₂ particles resulting from step (a).
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16. A process for preparing a TiO₂ pigment, comprising the steps of:

(a) precipitating a hydrous oxide selected from the group consisting of silica, alumina, zirconia, and mixtures thereof onto the surfaces of TiO₂ particles to form surface-coatings, and
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(b) mixing a slurry of the surface-coated TiO₂ particles with reagents to form in-situ substantially discrete inorganic particles having an average diameter size within the range of about 5 to about 100 nm, wherein the inorganic particles are dispersed onto the surface-coated TiO₂ particles in an amount of less than 20 wt.% based on total pigment weight.
45

17. A process for preparing a TiO₂ pigment slurry, comprising the steps of:

(a) preparing finished TiO₂ particles having a surface-coating comprising a hydrous oxide selected from the group consisting of silica, alumina, zirconia, and mixtures thereof; and
50

(b) mixing the finished TiO₂ particles with an aqueous mixture comprising a colloidal suspension of inorganic particles and dispersant, wherein the TiO₂ particles and the colloidal particles are both above or below their respective isoelectric points, to form substantially discrete inorganic particles having an average diameter size within the range of about 5 to about 100 nm which are dispersed onto the surfaces of the TiO₂ particles in an amount of less than 20 wt.% based on total pigment weight.
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Patentansprüche

1. TiO_2 -Pigment, im wesentlichen bestehend aus TiO_2 -Partikeln, die aufweisen: (a) weitgehend diskrete anorganische Partikel mit einem mittleren Durchmesser im Bereich von etwa 5 bis etwa 100 nm, die in einer Menge von weniger als 20 Gewichtsprozent, bezogen auf das Gesamtgewicht des Pigments, auf den Oberflächen der TiO_2 -Partikel dispergiert sind; (b) eine Deckbeschichtung aus einem hydratisierten Oxid, ausgewählt aus der Gruppe, bestehend aus Siliciumdioxid, Aluminiumoxid, Zirkoniumoxid und Mischungen davon.
2. TiO_2 -Pigment, im wesentlichen bestehend aus TiO_2 -Partikeln, die aufweisen: (a) eine Oberflächenbeschichtung aus einem hydratisierten Oxid, ausgewählt aus der Gruppe, bestehend aus Siliciumdioxid, Aluminiumoxid, Zirkoniumoxid und Mischungen davon; und (b) weitgehend diskrete anorganische Partikel mit einem mittleren Durchmesser im Bereich von etwa 5 bis etwa 100 nm, die in einer Menge von weniger als 20 Gewichtsprozent, bezogen auf das Gesamtgewicht des Pigments, auf der Oberfläche der hydratisierten Oxid-Oberflächebeschichtung dispergiert sind.
3. TiO_2 -Pigment nach Anspruch 1 oder 2, wobei die anorganischen Partikel ausgewählt sind aus der Gruppe, bestehend aus Oxiden von Silicium, Titan, Zirkonium, Zink, Magnesium, Aluminium, Yttrium, Antimon, Cer und Zinn; aus Sulfaten von Barium und Calcium; aus Sulfiden von Zink; aus Carbonaten von Zink, Calcium, Magnesium, Blei und gemischten Metallen; aus Nitriden von Aluminium; aus Phosphaten von Aluminium, Calcium, Magnesium, Zink und Cer; aus Titanaten von Magnesium, Calcium und Aluminium; aus Fluoriden von Magnesium und Calcium; aus Silicaten von Zink, Zirkonium, Calcium, Barium, Magnesium, gemischten Erdalkalimetallen und natürlich vorkommenden Silicat-Mineralien; aus Alumosilicaten von Alkali- und Erdalkalimetallen; aus natürlich vorkommenden Alumosilicaten; Aluminaten von Zink, Calcium, Magnesium und gemischten Erdalkalimetallen; aus Hydroxiden von Aluminium; aus Diamant; sowie aus Mischungen oder Compositen der vorgenannten Partikel.
4. TiO_2 -Pigment nach Anspruch 1 oder 2, wobei die anorganischen Partikel einen mittleren Durchmesser im Bereich von 7 bis 50 nm haben.
5. TiO_2 -Pigment nach Anspruch 1 oder 2, wobei die Menge anorganischer Partikel bis zu 15 Gewichtsprozent und die Menge hydratisierter Oxide bis zu 16 Gewichtsprozent beträgt, bezogen auf das Gesamtgewicht des Pigments.
6. TiO_2 -Pigment nach Anspruch 1 oder 2, wobei die Menge anorganischer Partikel bis zu 10 Gewichtsprozent und die Menge hydratisierter Oxide bis zu 16 Gewichtsprozent beträgt, bezogen auf das Gesamtgewicht des Pigments.
7. TiO_2 -Pigment nach Anspruch 6, wobei die anorganischen Partikel ausgewählt werden aus der Gruppe, bestehend aus Siliciumdioxid, Aluminiumoxid, Calciumcarbonat und Mischungen oder Compositen davon.
8. TiO_2 -Pigment nach Anspruch 7, wobei das Pigment eine Ölabsorption von weniger als 35 hat.
9. TiO_2 -Pigment nach Anspruch 1 oder 2, wobei die anorganischen Partikel Siliciumdioxid-Partikel in einer Menge bis zu 10 Gewichtsprozent, bezogen auf das Gesamtgewicht des Pigments, aufweisen und wobei die hydratisierten Oxide bis zu 4 Gewichtsprozent Siliciumdioxid und bis zu 3 Gewichtsprozent Aluminiumoxid, bezogen auf das Gesamtgewicht des Pigments, aufweisen.
10. TiO_2 -Pigment nach Anspruch 9, wobei das Pigment eine Ölabsorption von weniger als 25 hat.
11. TiO_2 -Pigment nach Anspruch 9, wobei das Pigment einen Lichtstreckkoeffizienten größer als $0,31 \text{ m}^2/\text{g}$ bei einer Volumenkonzentration des Pigments von 25 Prozent hat und größer als $0,26 \text{ m}^2/\text{g}$ bei einer Volumenkonzentration des Pigments von 35 Prozent hat.
12. TiO_2 -Pigmentaufschlämmung umfassend das TiO_2 Pigment nach Anspruch 1 oder 2, wobei die Aufschlämmung einen Feststoffgehalt an TiO_2 -Pigment oberhalb von 50 Gewichtsprozent hat.
13. Verfahren zum Herstellen von TiO_2 -Pigment, umfassend die Schritte:
 - (a) Mischen der Aufschlämmung von TiO_2 -Partikeln mit einer kolloidalen Suspension von anorganischen Partikeln, wobei sich die TiO_2 -Partikel und die kolloidalen Partikel beide oberhalb oder unterhalb ihrer entsprechenden isoelektrischen Punkte befinden, so daß weitgehend diskrete anorganische Partikel mit einem mitt-

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leren Durchmesser im Bereich von etwa 5 bis etwa 100 nm auf den Oberflächen der TiO_2 -Partikel in einer Menge von weniger als 20 Gewichtsprozent, bezogen auf das Gesamtgewicht des Pigments, dispergiert werden; sowie

(b) Abscheiden eines hydratisierten Oxids, ausgewählt aus der Gruppe, bestehend aus Siliciumdioxid, Aluminiumoxid, Zirkoniumoxid und Mischungen davon, auf den aus Schritt (a) resultierenden TiO_2 -Partikeln.

14. Verfahren zum Herstellen eines TiO_2 -Pigments, umfassend die Schritte:

(a) Abscheiden eines hydratisierten Oxids, ausgewählt aus der Gruppe, bestehend aus Siliciumdioxid, Aluminiumoxid, Zirkoniumoxid und Mischungen davon, auf den Oberflächen der TiO_2 -Partikel, um Oberflächenbeschichtungen zu erzeugen; sowie

(b) Mischen einer Aufschlämmung der oberflächenbeschichteten TiO_2 -Partikel mit einer kolloidalen Suspension von anorganischen Partikeln, wobei sich die TiO_2 -Partikel und die kolloidalen Partikel beide oberhalb oder unterhalb ihrer entsprechenden isoelektrischen Punkte befinden, so daß weitgehend diskrete anorganische Partikel mit einem mittleren Durchmesser im Bereich von etwa 5 bis etwa 100 nm auf den oberflächenbeschichteten TiO_2 -Partikeln in einer Menge von weniger als 20 Gewichtsprozent, bezogen auf das Gesamtgewicht des Pigments, dispergiert werden.

15. Verfahren zum Herstellen eines TiO_2 -Pigments, umfassend die Schritte:

(a) Mischen einer Aufschlämmung von TiO_2 -Partikeln mit Reagentien zur in-situ-Erzeugung von weitgehend diskreten TiO_2 -Partikeln mit einem mittleren Durchmesser im Bereich von etwa 5 bis etwa 100 nm, wobei die anorganischen Partikel auf der Oberfläche der TiO_2 -Partikel in einer Menge von weniger als 20 Gewichtsprozent, bezogen auf das Gesamtgewicht des Pigments, dispergiert werden; und

(b) Abscheiden eines hydratisierten Oxids aus der Gruppe, bestehend aus Siliciumdioxid, Aluminiumoxid, Zirkoniumoxid und Mischungen davon, auf den aus Schritt (a) resultierenden TiO_2 -Partikeln.

16. Verfahren zum Herstellen eines TiO_2 -Pigments, umfassend die Schritte:

(a) Abscheiden eines hydratisierten Oxids, ausgewählt aus der Gruppe, bestehend aus Siliciumdioxid, Aluminiumoxid, Zirkoniumoxid und Mischungen davon, auf den TiO_2 -Partikeln zur Erzeugung von Oberflächenbeschichtungen;

(b) Mischen einer Aufschlämmung der oberflächenbeschichteten TiO_2 -Partikel mit Reagentien zur in-situ-Erzeugung von weitgehend diskreten TiO_2 -Partikeln mit einem mittleren Durchmesser im Bereich von etwa 5 bis etwa 100 nm, wobei die anorganischen Partikel auf den oberflächenbeschichteten TiO_2 -Partikeln in einer Menge von weniger als 20 Gewichtsprozent, bezogen auf das Gesamtgewicht des Pigments, dispergiert werden.

17. Verfahren zum Herstellen einer TiO_2 -Pigmentaufschlämmung, umfassend die Schritte:

(a) Herstellen von fertigen TiO_2 -Partikeln mit einer Oberflächenbeschichtung, die ein hydratisiertes Oxid aufweist, ausgewählt aus der Gruppe, bestehend aus Siliciumdioxid, Aluminiumoxid, Zirkoniumoxid und Mischungen davon; sowie

(b) Mischen der fertigen TiO_2 -Partikel mit einer wässrigen Mischung, die eine kolloidale Suspension von anorganischen Partikeln und Dispergiernmittel aufweist, wobei sich die oberflächenbeschichteten TiO_2 -Partikel und die kolloidalen Partikel beide oberhalb oder unterhalb ihrer entsprechenden isoelektrischen Punkte befinden, um weitgehend diskrete anorganische Partikel mit einem mittleren Durchmesser im Bereich von etwa 5 bis etwa 100 nm zu erzeugen, die auf den Oberflächen der TiO_2 -Partikel in einer Menge von weniger als 20 Gewichtsprozent, bezogen auf das Gesamtgewicht des Pigments, dispergiert sind.

Revendications

1. Pigment de TiO_2 constitué essentiellement de particules de TiO_2 comportant (a) des particules inorganiques subs-

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lantiellement discrètes, avec une taille de diamètre moyen dans le domaine allant d'environ 5 à environ 100 nm, dispersées sur les surfaces des particules de TiO_2 selon une quantité ne dépassant pas 20% en poids, sur la base du poids total du pigment, et (b) une couche supérieure comprenant un oxyde hydraté choisi dans le groupe constitué de silice, d'alumine, de zircone et de mélanges de celles-ci.

2. Pigment de TiO_2 constitué essentiellement de particules de TiO_2 comportant (a) un revêtement de surface comprenant un oxyde hydraté choisi dans le groupe constitué de silice, d'alumine, de zircone et de mélanges de celles-ci, et (b) des particules inorganiques substantiellement discrètes, avec une taille de diamètre moyen dans le domaine allant d'environ 5 à environ 100 nm, qui sont dispersées sur la surface du revêtement de surface à base d'oxyde hydraté selon une quantité ne dépassant pas 20% en poids, sur la base du poids total du pigment.
3. Pigment de TiO_2 suivant la revendication 1 ou 2, dans lequel les particules inorganiques sont choisies dans le groupe constitué d'oxydes de silicium, de titane, de zirconium, de zinc, de magnésium, d'aluminium, d'yttrium, d'antimoine, de cérium et d'étain; de sulfates de baryum et de calcium; de sulfures de zinc; de carbonates de zinc, de calcium, de magnésium, de plomb et de métaux mixtes; de nitrures d'aluminium; de phosphates d'aluminium, de calcium, de magnésium, de zinc et de cérium; de titanates de magnésium, de calcium et d'aluminium; de fluorures de magnésium et de calcium; de silicates de zinc, de zirconium, de calcium, de baryum, de magnésium, de métaux alcalino-terreux mixtes et de silicates minéraux d'origine naturelle; d'aluminosilicates de métaux alcalins et alcalino-terreux; d'aluminosilicates d'origine naturelle; d'aluminates de zinc, de calcium, de magnésium et métaux alcalino-terreux mixtes; d'hydroxydes d'aluminium; de diamant; et de mélanges ou de composites des particules précédentes.
4. Pigment de TiO_2 suivant la revendication 1 ou 2, dans lequel les particules inorganiques présentent une taille de diamètre moyen dans le domaine allant de 7 à 50 nm.
5. Pigment de TiO_2 suivant la revendication 1 ou 2, dans lequel la quantité de particules inorganiques va jusqu'à 15% en poids et la quantité d'oxydes hydratés va jusqu'à 16% en poids, sur la base du poids total du pigment.
6. Pigment de TiO_2 suivant la revendication 1 ou 2, dans lequel la quantité de particules inorganiques va jusqu'à 10% en poids et la quantité d'oxydes hydratés va jusqu'à 16% en poids, sur la base du poids total du pigment.
7. Pigment de TiO_2 suivant la revendication 6, dans lequel les particules inorganiques sont choisies dans le groupe constitué de silice, d'alumine, de carbonate de calcium et de mélanges ou de composites de ceux-ci.
8. Pigment de TiO_2 suivant la revendication 7, dans lequel le pigment présente une prise d'huile ne dépassant pas 35.
9. Pigment de TiO_2 suivant la revendication 1 ou 2, dans lequel les particules inorganiques comprennent des particules de silice selon une quantité allant jusqu'à 10% en poids, sur la base du poids total du pigment, et les oxydes hydratés comprennent jusqu'à 4% en poids de silice et jusqu'à 3% en poids d'alumine, sur la base du poids total du pigment.
10. Pigment de TiO_2 suivant la revendication 9, dans lequel le pigment présente une prise d'huile ne dépassant pas 25.
11. Pigment de TiO_2 suivant la revendication 9, dans lequel le pigment présente un coefficient de dispersion de la lumière supérieur à $0,31 \text{ m}^2/\text{g}$ à une concentration pigmentaire volumique de 25% et supérieur à $0,26 \text{ m}^2/\text{g}$ à une concentration pigmentaire volumique de 35%.
12. Dispersion de pigment de TiO_2 comprenant le pigment de TiO_2 suivant la revendication 1 ou 2, dans laquelle la dispersion contient une teneur en solides de pigment de TiO_2 au-dessus de 50% en poids.
13. Procédé de préparation d'un pigment de TiO_2 , comprenant les étapes:
 - (a) de mélange d'une dispersion de particules de TiO_2 avec une suspension colloïdale de particules inorganiques, mélange dans lequel les particules de TiO_2 et les particules colloïdales se trouvent à la fois au-dessus ou en dessous de leurs points isoélectriques respectifs, de sorte que des particules inorganiques substantiellement discrètes avec une taille de diamètre moyen dans le domaine allant d'environ 5 à environ 100 nm sont dispersées sur les surfaces des particules de TiO_2 selon une quantité ne dépassant pas 20% en poids, sur la base du poids total du pigment; et

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(b) de précipitation d'un oxyde hydraté choisi dans le groupe constitué de silice, d'alumine, de zircon et de mélanges de celles-ci sur les particules de TiO_2 résultant de l'étape (a).

14. Procédé de préparation d'un pigment de TiO_2 , comprenant les étapes:

(a) de précipitation d'un oxyde hydraté choisi dans le groupe constitué de silice, d'alumine, de zircon et de mélanges de celles-ci sur les surfaces des particules de TiO_2 pour former des revêtements de surface, et
(b) de mélange d'une dispersion de particules de TiO_2 revêtues en surface avec une suspension colloïdale de particules inorganiques, mélange dans lequel les particules de TiO_2 et les particules colloïdales se trouvent à la fois au-dessus ou en dessous de leurs points isoélectriques respectifs, de sorte que les particules inorganiques substantiellement discrètes avec une taille de diamètre moyen dans le domaine allant d'environ 5 à environ 100 nm sont dispersées sur les particules de TiO_2 revêtues en surface selon une quantité ne dépassant pas 20% en poids, sur la base du poids total du pigment.

15. Procédé de préparation d'un pigment de TiO_2 , comprenant les étapes:

(a) de mélange d'une dispersion de particules de TiO_2 avec des réactifs pour former in-situ des particules inorganiques substantiellement discrètes avec une taille de diamètre moyen dans le domaine allant d'environ 5 à environ 100 nm, mélange dans lequel les particules inorganiques sont dispersées sur les surfaces des particules de TiO_2 selon une quantité ne dépassant pas 20% en poids, sur la base du poids total du pigment; et
(b) de précipitation d'un oxyde hydraté choisi dans le groupe constitué de silice, d'alumine, de zircon et de mélanges de celles-ci sur les particules de TiO_2 résultant de l'étape (a).

16. Procédé de préparation d'un pigment de TiO_2 , comprenant les étapes:

(a) de précipitation d'un oxyde hydraté choisi dans le groupe constitué de silice, d'alumine, de zircon et de mélanges de celles-ci sur les surfaces des particules de TiO_2 pour former des revêtements de surface; et
(b) de mélange d'une dispersion de particules de TiO_2 revêtues en surface avec des réactifs pour former in-situ des particules inorganiques substantiellement discrètes avec une taille de diamètre moyen dans le domaine allant d'environ 5 à environ 100 nm, mélange dans lequel les particules inorganiques sont dispersées sur les particules de TiO_2 revêtues en surface selon une quantité ne dépassant pas 20% en poids, sur la base du poids total du pigment.

17. Procédé de préparation d'une dispersion de pigment de TiO_2 , comprenant les étapes:

(a) de préparation de particules de TiO_2 finies avec un revêtement de surface comprenant un oxyde hydraté choisi dans le groupe constitué de silice, d'alumine, de zircon et de mélanges de celles-ci; et
(b) de mélange des particules de TiO_2 finies avec un mélange aqueux comprenant une suspension colloïdale de particules inorganiques et d'un agent dispersant, mélange dans lequel les particules de TiO_2 et les particules colloïdales se trouvent à la fois au-dessus ou en dessous de leurs points isoélectriques respectifs, pour former des particules inorganiques substantiellement discrètes avec une taille de diamètre moyen dans le domaine allant d'environ 5 à environ 100 nm, qui sont dispersées sur les surfaces des particules de TiO_2 selon une quantité ne dépassant pas 20% en poids, sur la base du poids total du pigment.